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TITLE: Reactions of 4-hydroxy-2(E)-nonenal and related aldehydes with proteins studied by carbon-13 nuclear magnetic resonance spectroscopy.
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AB In order to understand the modifications of proteins produced by aldehydes
of lipid peroxidation, [1-13C]-2(E)-hexenal, [1-13C]-4- oxopentanal, and a
mixture of [1-13C]- and [2-13C]4-hydroxynon-2(E)-enal were synthesized and
the reaction of each of the labeled aldehydes with bovine serum albumin was analyzed by 13C NMR spectroscopy. Protein nucleophiles add to the 3-position of hexenal, and the resulting propanal moieties appear to undergo aldol condensation, form imine cross-links with lysyl residues, or
lead to pyridinium rings. During the reaction of 4- oxopentanal with the lysyl residues of bovine serum albumin, only 1-alkyl-2- methylpyrrole and a possible intermediate leading to the pyrrole were observed. Hydroxy-pyrrolidine cross-links such as 25 could not be detected, leaving the pyrrole as the mediator of protein **cross**-linking. The **Michael** adducts are the major products in the reaction between 4-hydroxynon-2-enal and proteins. They exist almost exclusively in the cyclic hemiacetal form and do not appear to cross-link through imine formation with lysyl residues. A minor pathway involves the reaction of 4-hydroxynon-2-enal with the lysyl amino groups of protein resulting in 2-pentylpyrrole adducts that may mediate protein **cross**-linking. The **Michael** adducts appear not to be the direct source of the pyrrole, but the imine 32 and the enamine 35 are likely intermediates toward the five-membered ring.

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